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Magnesia Bricks for Lining Cement Kilns.

THE following is a translation of an article in *La Revue des Matériaux de Construction et de Travaux Publics* by M. Felix Krémer.

Although alumina bricks behaved very well in the preheating and cooling sections of rotary or shaft cement kilns, in the clinker-forming zone, where, apart from the high temperature and the mechanical action of the charge, the chemical action of the clinker during formation and the action of the ashes destroy the lining, the use of alumina bricks is not very satisfactory, especially in rotary kilns. In the clinker-forming zone of rotary kilns first-quality bricks with a content of 40 to 42 per cent. of alumina only last from two to four months. If there are exceptional cases, where the bricks have lasted six to twelve months or even longer, this only happens in rotary kilns worked under specially favourable conditions and where they are not overdriven. In the clinker-forming zone of shaft kilns a lining of alumina bricks is usually more resistant than in rotary kilns, and the lining frequently lasts for a whole season. It is well known, however, that in shaft kilns the adhesion of the charge to the lining is very obnoxious, and this is the great disadvantage of alumina bricks. Owing to the low resistance of alumina bricks in the clinker-forming zone of rotary kilns and the repeated clinging of the charge to the lining in shaft kilns the need arose for a more durable and suitable lining of cement kilns, particularly since the specifications for the quality of cement have become more and more strict and made the working conditions of the kilns more severe.

Clinker Bricks.

The search for an improvement of the lining in the clinker formation zone led to the use of cement clinker bricks, invented by Dr. Valeur, and these are still in use in spite of their disadvantages. The life of clinker bricks is about four to six weeks and reaches a maximum of four months. It seems very difficult

to get a product of this kind with a longer life than four months, since clinker bricks have only a very low resistance against variations of temperature and insufficient refractory properties. Further, the chemical and physical changes which occur in the concrete while it is being heated up to the burning temperature have an injurious effect on them.

High-Alumina Bricks.

The introduction of bricks with a very high alumina content, known as bauxite or corindon bricks, and which contain 50 to 70 per cent. of alumina (in exceptional cases more than 90 per cent.) was a notable step in the supply of improved linings for the clinker-forming section. All products with a high alumina content have a high resistance to variations of temperature and an improved resistance against the chemical action of the clinker and ashes. Moreover, in addition to their greater durability against mechanical action and their superior refractory power, they last longer than bricks made of chamotte or clinker.

Notwithstanding the undoubted improvements obtained by using bricks with a large alumina content, they did not satisfy all the conditions. Bricks with a high alumina content have a sufficient refractory power and their resistance to chemicals is much superior to ordinary alumina bricks. Nevertheless, they are far from fulfilling all the requirements of the cement kiln, since, by comparison with clinker rich in lime, they have a notable acid character. After the rejection of clinker bricks, the investigation turned to the alkaline refractory product, magnesia, which had been used with success in metallurgical furnaces subjected to the most severe conditions. This highly basic product, which has a greater thermal resistance than any other refractory material, has long been considered the ideal material from a chemical point of view for lining the clinker-forming zone of cement kilns. But bricks of normal magnesia have little resistance to variations in temperature, and this was an obstacle to their introduction in the cement industry. After several years' experience in the laboratory and in practice many of the disadvantages incidental to ordinary magnesia bricks have been removed. Special magnesia bricks, which are superior to alumina and high-alumina bricks in regard to resistance against temperature, have been made, and are now available.

Following the manufacture of bricks of special magnesia, suitable for cement kilns, it was necessary to overcome the many difficulties in introducing the new product on a large scale in the cement industry. Foremost was the dislike of the cement manufacturer for materials which contain magnesia. This is based on the well-known tendency of cement rich in magnesia to expand. In most countries the maximum content of magnesia in cement is restricted by specification. Actually the fear of an absorption of considerable quantities of magnesia by the cement is not justified, because even under the assumption of a total consumption of the lining it would be less than one-hundredth of 1 per cent. of the clinker.

The question of the lining caused another difficulty, since the high thermal expansion of magnesia bricks fractured the steel shell of the kiln, because the lining was fixed too rigidly and with too tight joints. This question has been solved

by making the bricks of a certain form and in small sizes, and by laying and fixing them in a special manner. Nowadays there are mainly two methods of laying the bricks, viz., (1) laid dry with flat pieces of steel and cardboard between the joints ; and, (2) laid with a wire mesh and a mortar of magnesium silicate. Both methods have given good results in metallurgical furnaces, but time was required to make an absolutely successful lining for cement kilns. The steel sheets, the cardboard, and the wire mesh in the joints are all to allow expansion of the bricks due to temperature. At the fusion temperature of cement, that is, about 1450 deg. C., magnesia bricks undergo an expansion of about 1.7 per cent. of their length when cold. The expansions in percentage of the initial length are 0.1 at 200 deg. C., 0.7 at 700 deg. C., and 1.67 at 1400 deg. C.

In kilns with an outer steel shell the cardboard or wire mesh should be designed to give enough free space to allow for the expansion of the bricks when the kiln is hot. Laying the bricks with cardboard spaces is to be preferred to using the steel flats, because the steel melts under the heat and forms with the bricks a ferrite of magnesia, which is very refractory and which binds the bricks together. The same happens when wire mesh is used. Meanwhile, however, the mortar of magnesia and silicate cements the bricks in the cold state. But if cardboard is used cementing does not take place in the cold state, for it burns and disintegrates the brickwork.

Cement makers often object that laying special magnesia bricks would be too complicated. This fear will, however, be quickly abandoned by anyone who watches bricks being laid dry in a rotary kiln and observes with what speed the work proceeds. For some time experiments have been going on to find a process of bricklaying in which only mortar is used, and it seems as if these experiments are leading to a favourable result.

At first the thermal conductivity of magnesia bricks was troublesome, as the steel shell of the rotary kiln reddened with heat before the protective crust formed. As, however, the protective crust forms satisfactorily on most of the magnesia bricks, the redness of the shell disappeared after several days. Nevertheless, the shell of the kiln remained at a relatively high temperature under continuous working, and outer isolating linings were tried. However, a considerable reduction of the thermal conductivity of the magnesia has been made and some of these bricks can be used without any outer lining.

The special magnesia bricks proved to be very successful for cement kilns. In addition to their long life their refractory power allows work at much higher temperatures, which increases the output and improves the quality of the clinker. Due to the chemical composition of magnesia bricks they can have no influence on the formation of rings. In plants where rings form frequently a trial of special magnesia bricks should be made. As it is almost impossible for the kiln charge to cling to the lining, magnesia bricks are very suitable for shaft kilns. The passage of the charge goes on without hindrance and a uniform clinker is obtained.

Experience has shown that in shaft kilns the various kinds of magnesia bricks do not behave in the same uniformly favourable manner. The conditions of manu-

facture, such as the size of the grains of magnesia, the pressure, and the degree of burning play their parts in the behaviour of the bricks. Smoothness of surface, a high mechanical resistance, and burning as hard as possible favour the good behaviour of the bricks, which is also a function of the composition of the raw magnesia. It has happened, for instance, that magnesia bricks in the upper part of a shaft kiln have been destroyed prematurely by wet, but this cannot happen if first-quality material and approved methods of making have been used in their manufacture.

Nowadays it is possible to manufacture bricks of special magnesia which have the greatest resistance to wetness. They consist mainly of natural magnesia, rich in iron, and they give, when properly burned, bricks which are mostly composed of a crystalline periclase insensitive to wetness.

The main conditions which good special bricks for the cement industry should fulfil are :

(1) Very high resistance against the chemical action of the alkaline clinker.
(2) Very high refractory power ; the melting point must be more than 2000 deg. C. (higher than Seger mark 42).
(3) Great resistance against the action of the hot charge in the kiln. Temperature at the beginning of the melting of the charge must be about 1500 deg. C. Temperature at the time of melting must be 1600 deg. C.

(4) Very great resistance against variations of temperature ; about 100 changes of temperature under compressed air for a brick heated to 950 deg. C.

(5) Resistance in a cold state against compression must be more than 2,500 lb. per square inch.

(6) No shrinkage after heating to a temperature of 1500 deg. C.

(7) Lowest thermal conductivity not more than $\frac{2 \text{ kg. cal.}}{m \text{ h deg. C.}}$ at 700 deg. C.

(8) Good resistance against wetness.

(9) Shape and form regular ; corners and arrises sharp.

Tests made with commercially available special magnesia bricks showed important differences in their results. The tests were made for resistance against variations of temperature, resistance against the action of the hot kiln charge, for shrinkage, and for thermal conductivity. For this reason it is advisable to order the special bricks to comply with a definite specification.

Solubility of Cements.

A SERIES of tests on the solubility of cements are described by Dr. F. C. Lea in the Technical Paper No. 26 of the Building Research Board (H.M. Stationery Office. Price 6d). The solubility of cements is a factor requiring consideration in connection with the deterioration of concrete dams exposed to the action of pure and slightly acid natural waters. It is commonly observed that in dams which have become leaky a deposit of lime is found on the down-stream face. The primary cause of deterioration is the permeability of the concrete, but the extraction of lime from the cement and its removal in solution eventually increase the rate of decay. When the water impounded behind a dam is hard the amount of leaching is not usually serious, and, indeed, lime may even be deposited from the water rather than removed by it in solution. With soft waters, however, such as are common in many mountain areas, solution of the lime may become a serious factor and many instances of decay of this type have been reported. The methods used for comparing the solubilities of set cements may be divided into three main classes : (1) Extraction tests on set cement, (2) percolation tests on mortars and concretes, and (3) surface solution tests on mortars and concretes. These are discussed in the report in the light of the experimental work described, and it is concluded that the extraction test gave the most satisfactory results. This test was as follows :

Cubes with 50-sq. cm. faces, made of neat cement gauged with 28 per cent. of water by weight, were cured for three days in moist air at 18 deg. C. and then in water at 18 deg. C. until one or three months old. The set cement was crushed and a fraction of grain size 0.21 to 0.09 mm. (British standard sieves Nos. 72 and 170) was used for the test. A 1-g. sample was then extracted with fifteen successive volumes (20 c.c. each) of distilled water, as described by Werner,⁽¹⁾ and the filtrates from each five successive extractions combined and the lime in solution estimated. The loss on ignition of the set cement was determined, and the total amount of lime extracted calculated as g. CaO per g. anhydrous cement. This method proved simple to carry out, and a satisfactory reproducibility was obtained between triplicate determinations on specimens from three separate neat cement cubes. The maximum range of three determinations was about 15 per cent. and the average range about 7 per cent. of the mean.

⁽¹⁾ WERNER, D. A Comparative Investigation of the Solubility in Water of Three Different Cements. *Zement*, 1931, **20**, 626.

Improvement in Clinker Grinding

THE improvement in the quality of cement due to the use of more efficient plant during the past twenty years is briefly described in a recent number of *Concrete*. In the course of this review reference is made to a separate mill, known as a "preliminator," of Allis-Chalmers manufacture, which performs the functions of the coarse-grinding, or first, compartment of a compartment mill.

A typical flow sheet illustrating the use of this principle of clinker grinding is shown in *Fig. 1*. The clinker enters the feed end of the preliminator, and from the discharge end of this unit the ground material is conveyed to a screen with which this preliminary grinding unit is operated in closed circuit. Here the material is passed through a 20-mesh screen, the product coarser than 20-mesh being returned to the preliminator for further grinding. The product passing the screen is conveyed to bins serving three-compartment mills in the

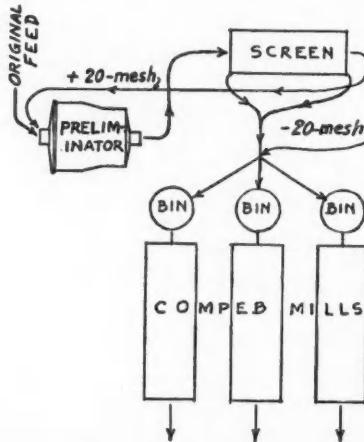


Fig. 1.—Flow-sheet of Typical Clinker-grinding Department in which the new Preliminary Grinding Unit is Incorporated.

typical installation shown. From these bins the material is fed to the compartment mills as required.

The new preliminary grinding unit is shown in some detail in *Fig. 2*. The outside diameter of this particular unit is 9ft. 6in. at the feed end, and 8ft. at the discharge end, and the inside length is 10ft. It is driven by a 400-h.p. motor. It is constructed with either a central or a peripheral discharge for operation with a separate vibrating screen, or with an outside screen similar to the kind supplied for compeb mills. The mechanical design is similar to that of compeb mills.

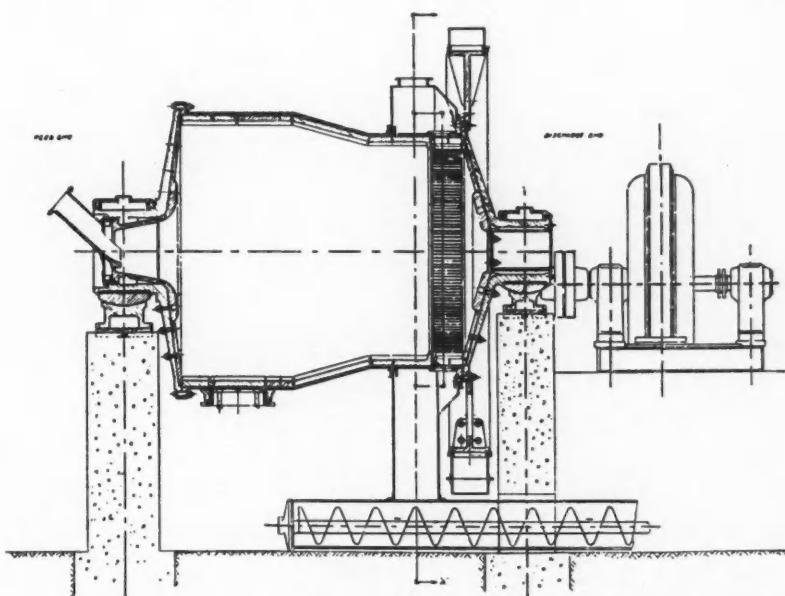


Fig. 2.—Detail of New Preliminary Clinker-Grinding Unit (see facing page).

Recent Patents Relating to Cement.

Hydraulic Cements.

496,669. C. E. Every (F. L. Smith and Co. Aktieselskab). June 4, 1937.

In the preparation of starting materials for the manufacture of cement a method of obtaining a fraction containing a high proportion of CaCO_3 comprises subjecting the starting materials to the action of a mill equipped with grinding elements consisting of metal cores with soft resilient coverings, separating the ground material into fractions, and eliminating the fraction that is lower in CaCO_3 . The mill may be a roller mill with rubber-covered rollers, a tube mill with rubber covered grinding bodies, or a hammer mill with rubber-coated hammers, and the covering may consist of pure vulcanised rubber at least 3 mm. thick. When the starting material consists of impure limestone, clay and sand the coarse fraction contains the higher proportion of CaCO_3 and if a still higher proportion is desired the coarse fraction

is subjected to flotation. In cases where the CaCO_3 is present in a soft component and will be concentrated in the fine fraction, then the coarse fraction is eliminated.

Concrete Improver.

504,259. J. M. Beau. October 18, 1938.

Finely divided magnetic oxide of iron, Fe_3O_4 , is added to cement, e.g. Portland, natural or aluminous cement, or is incorporated in cement concretes or mortars at the time of mixing, to improve the properties, e.g. the impermeability, strength, and resistance to wear and corrosion of the resulting concrete or mortar. The amount used is preferably between 5 and 35 per cent. of the weight of the cement, but may be as high as 100 per cent. The oxide used is preferably the artificial magnetite produced by the reduction of sesquioxide of iron from residues produced in the roasting of iron pyrites.

Constitution of Portland Cement Clinker

(Continued from October number.)

By R. H. BOGUE

Equilibrium Crystallisation.

The chemical nature of a Portland cement clinker is not defined by stating its oxide composition but by stating the proportions and character of the individual substances which may be present and which are referred to as "phases." Investigation of the conditions under which the various phases can exist in equilibrium with one another under any specified conditions of temperature and pressure is a necessary step in arriving at an understanding of the essential nature, that is, the chemical constitution, of clinker.

Recent work has indicated that, in the process of manufacturing Portland cement clinker, complete crystalline equilibrium is not necessarily attained and that the presence of glass as one of the phases must be taken into consideration when investigating the constitution of the clinker. Knowledge of phase equilibria is necessary, however, in determining the phenomena which will occur even when crystalline equilibrium is not attained. It is necessary, therefore, to continue the phase equilibria investigations with this in mind. It is of importance in arriving at a knowledge of the constitution of clinker that we obtain and analyse information on the course followed in the development of the cement compounds as they are normally found in commercial operations. But the first step in this undertaking is a study under the ideal conditions which obtain with only a selected number of the compounds and with heat-treatments such that equilibrium conditions are at all times maintained. Such studies have been completed for several of the systems of Portland cement and are still being made for other systems.

The Clinker Compounds.—The publication by Rankin and Wright⁸ of the system $\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2$ in 1915 marked the beginning of a period of extraordinary activity in research by the methods of high-temperature phase equilibria. In a compilation by Hall and Insley³⁸ of phase diagrams of interest to the silicate technologist, published up to 1933, 47 binary and 32 ternary systems are listed together with 32 sections of 3-component systems. In the intervening five years about 75 additional diagrams have appeared which are now being compiled for publication by the same authors.

Rankin and Wright showed that, in mixtures of CaO , Al_2O_3 and SiO_2 of the general composition of Portland cement clinker, there exist at complete equilibrium crystallisation $3\text{CaO}\text{-}\text{SiO}_2$, $2\text{CaO}\text{-}\text{SiO}_2$ and $3\text{CaO}\text{-}\text{Al}_2\text{O}_3$.

³⁴ BROWNMILLER, L. T., & BOGUE, R. H. *Am. J. Sci.*, 1930, (5), 20, 241.

³⁵ BROWNMILLER, L. T. *Am. J. Sci.*, 1938, (5), 35, 241.

³⁶ HARRINGTON, E. A. *J. Optical Soc. Am.*, 1928, 16, 211.

³⁷ MCPHERSON, D. R., & FORBRICH, L. R. *Ind. Eng. Chem. (Anal. Ed.)*, 1937, 9, 451.

³⁸ HALL, F. P., & INSLEY, H. *J. Am. Ceramic Soc.*, 1933, 16, 455.

The nature of the iron compound in clinker has been indicated by the identification, in the system $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, of the compound $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$,³⁹ by numerous confirmations of its existence in more complex systems⁴⁰ and by the direct identification of its presence in commercial clinker.³⁴

The magnesia has been found to remain uncombined in the presence of CaO , SiO_2 and Al_2O_3 in the region of Portland cement,⁴¹ but a slight amount of solid solution may occur with $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$,^{25, 27} whereby that compound is changed in colour from chocolate brown to black and the pleochroism is increased.

Study on the alkali compounds is still incomplete, but in the systems containing only CaO , Al_2O_3 , and the alkalis, the compounds $8\text{CaO} \cdot \text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3$,²⁹ and $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$,³² appear to be the stable phases in the region near the CaO vertex. However, if cooling is not too rapid, the $8\text{CaO} \cdot \text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3$ may form a solid solution series with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$,^{30, 31} so that, in a mixture of the two, only one phase may be present.

Thus in a Portland cement mixture consisting of the components CaO , Al_2O_3 , Fe_2O_3 , SiO_2 and MgO , on complete equilibrium crystallisation we should expect to find $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, MgO and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ containing a small amount of MgO in solid solution.

The Alkali Components.—It has been pointed out that a prismatic dark interstitial material is often observed in polished sections of clinker and that this phase appears to be associated with the alkalis inasmuch as it has not been observed, in laboratory clinkers, in the absence of soda and potash. Up to now the prismatic phase has not been definitely identified. Some evidence suggests that it may consist, so far as the soda component is concerned, of a ternary compound of CaO , Na_2O and Al_2O_3 or a solid solution of that compound with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and containing also small amounts of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. On the other hand, some indications suggest that silica also may be involved, both in the soda and in the potash compounds which constitute the prismatic phase.

The potash compound $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$, stable in the system $\text{CaO-Al}_2\text{O}_3\text{-K}_2\text{O}$, has been studied with $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$.³¹ It has been found that $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3\text{-K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ forms a binary system with no new compounds, having an eutectic at 81 per cent. $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ —19 per cent. $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ and melting at 1,343 deg. \pm 5 deg. The melting temperatures rise sharply on the potash side of the eutectic. The $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ apparently takes up some $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ in solid solution since there is a difference in pleochroism of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ on the addition of $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$, but the failure to observe changes in indices of refraction indicates that the amount of such solution is probably small. The $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ likewise takes up some $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ in solid solution as indicated by an increase in index of refraction from 1.603 to 1.625. The amount of this solution is also probably small, however, because the $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ does not lose its isotropism.

³⁹ HANSEN, C. W., BROWNMILLER, L. T., & BOGUE, R. H. *J. Am. Chem. Soc.*, 1928, 50, 396.

⁴⁰ LEA, F. M., & PARKER, T. W. *Phil. Trans. Roy. Soc.*, 1934, 234, I.—*Bld. Res. Techn., Paper, No. 16, 1935.*

⁴¹ HANSEN, C. W. *J. Am. Chem. Soc.*, 1928, 50, 3081.

An extension of this study to include the compounds $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ has been made using mixtures of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, up to 50 per cent. $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, with the addition of $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ up to 25 per cent. Throughout this region the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ form a continuous solid solution series and at any composition (within the range studied) the phase relations are those of a pseudo-binary system of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ - $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ solid solution plus $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$. The melting temperature of the lowest melting composition increases from 1,343 deg. (in the system $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ - $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$) to 1,357 deg. (in the mixture wherein the solid solution consists of equal parts of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$). The composition of the lowest-melting composition contains slightly decreasing amounts of $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ as the $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ content of the solid solution increases.

The dark prismatic material in laboratory clinkers containing CaO , Al_2O_3 , Fe_2O_3 , SiO_2 and K_2O , however, has optical characteristics different from those of $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ so it appears probable that some reaction occurs in such mixtures between the potash and the silica producing the compound of potash observed as prismatic dark interstitial material. A knowledge of the nature of that phase awaits completion of studies now under way on the compounds $3\text{CaO} \cdot \text{SiO}_2$, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$, Al_2O_3 and $2\text{CaO} \cdot \text{SiO}_2$, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$, CaO .

Calculation of Compounds at Crystalline Equilibrium.—With a knowledge of the phases formed at crystalline equilibrium from any given oxide composition, it is possible to calculate, within the systems explored, the potential compound composition of the product.^{42, 43} Such information is available for systems consisting of CaO , Al_2O_3 , Fe_2O_3 , SiO_2 and MgO in the region of Portland cement. It is recognised at the outset that such calculations cannot represent completely the true conditions of any commercial clinker both because of the presence in such clinker of components other than those listed, upon which adequate information is still lacking, and also because, in commercial clinker, a condition of complete crystalline equilibrium is rarely or never attained.

Through study of the compounds, individually and collectively, followed by the examination of laboratory and commercial cements of controlled or selected compositions, one finds, for example, that $3\text{CaO} \cdot \text{SiO}_2$ is the compound chiefly responsible for high early strength. If, then, one wishes to produce a high-early-strength cement, an obvious procedure is to use a mix that will give a high $3\text{CaO} \cdot \text{SiO}_2$ content. By the method of calculation described, the procedure for accomplishing this without impairment of other desirable properties is at once obvious. Such calculations have been found useful in the specification of cements for special purposes, such as high-early-strength cement, low-heat cement, modified cement and sulphate-resistant cement. Such computed values focus the attention of the chemist on the ultimate compounds which, through test, may be found to be desirable or undesirable and, with that information, point

⁴² BOGUE, R. H. *Ind. Eng. Chem. (Anal. Ed.)*, 1929, I, 192.

⁴³ DAHL, L. A. *Rock Products*, 1929, 32, No. 23, p. 50.

the way to a simple and direct solution of industrial problems. The method lacks precision, but is less cumbersome than the equally unprecise method of oxide percentages and ratios, and possesses the advantage of fundamental soundness. As new information on the state of the minor constituents in clinker and the course of crystallisation is revealed through research, such information, as a matter of course, is applied to a refinement of the procedure and new calculations must replace the old. Science does not stand still.

Arrested Crystallisation.

In the manufacture of Portland cement, temperatures are employed which cause a part of the charge to liquefy, and most of the reactions of clinker formation take place during the period while the liquid is present. The temperature of first liquid formation has been found¹⁵ to be about 1,280 deg., but commercial clinker is often burned at temperatures of 1,450 deg. or higher. At these temperatures there may be from a quarter to a third of the total charge present in the liquid state. All of the alumina and ferric oxide, the alkalis and probably other minor constituents, part of the magnesia, a considerable amount of lime and some silica are then present in the liquid.

If the clinker cools very slowly, further reactions may take place between the liquid and the solid phases and, on final solidification, a condition obtain of crystalline equilibrium. Again, at a somewhat more rapid rate of cooling, the liquid may crystallise independently of further reaction with the solid phases; in this case the final compound composition of the clinker may be different from that of equilibrium crystallisation. And, finally, with very rapid cooling, the liquid may solidify without crystallisation and be present in the clinker as a glass. It is probable that, in commercial clinker, the cooling rate is rarely or never so slow that complete equilibrium crystallisation obtains nor yet so rapid that all of the liquid solidifies as glass. It seems probable that some glass, but quite variable amounts, will be found in all commercial clinkers.

The splendid investigation by Lea and Parker¹⁶ on the quaternary system $\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{Fe}_2\text{O}_3\text{-}\text{SiO}_2$ has provided the information by which the amount and composition of liquid formed with any mix of these components (within the portion of the system bounded by $\text{CaO}\text{-}2\text{CaO}\cdot\text{SiO}_2\text{-}5\text{CaO}\cdot3\text{Al}_2\text{O}_3\text{-}4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$) at any temperature may be computed. This information has greatly stimulated further research on the glassy phase since, for the first time, compositions representative of the liquid phase in clinkers of different compositions within this four-component system may be prepared for study. The finding¹⁶ that 4 to 6 per cent. of MgO dissolves in the liquid of the above system having $\text{Al}_2\text{O}_3\text{:}\text{Fe}_2\text{O}_3$ ratios between 0.68 and 3.0, permits the inclusion of MgO as a fifth component in studies on the glassy phase.

Nature of the Glassy Phase.—The appearance of the glassy phase in polished sections of clinker as an amorphous grey interstitial material has already been described. The nature of this material has been further investigated by Brownmiller.³⁵ It was found that homogeneous glasses showing no evidence of orientation by optical or X-ray methods could be obtained only when very

small charges (0.1 g. or less), weighted with platinum, were instantaneously quenched by immersion in mercury. When somewhat larger charges were used and the quenching was rapid but not instantaneous, rearrangements were found to occur which, though not advanced to the condition represented by the formation of the equilibrium compounds, nevertheless gave a product which indicated periodicity. With yet slower cooling, the equilibrium compounds appeared.

The intermediate state, which we have designated the "metastable phase," was generally faintly birefracting, showed indices of refraction always uniformly higher than those of the true glasses of similar composition, and gave a strong X-ray diffraction pattern which, within the range studied, was independent of the composition. The startling observation was made that this pattern was nearly identical with the pattern of pure crystalline $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. This suggested that $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ might be present, though theoretically it should not exist in the charges examined even at crystalline equilibrium, and preparations were made containing no alumina whatsoever, but the resulting metastable phase gave the same X-ray pattern, as shown in *Plate VII*. Nor was the phase an unstable

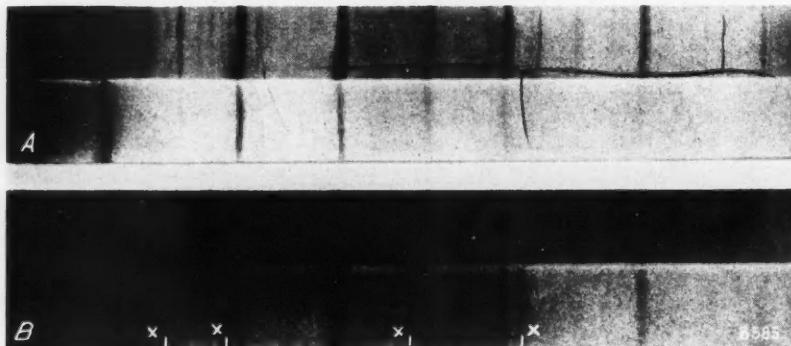


PLATE VII.—X-ray pattern of crystalline $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and quenched-liquid compositions.

(A) Upper—Pattern of crystalline $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Lower—Pattern of composition consisting of 53.9% of CaO , 15.3% of Al_2O_3 , 6.8% of SiO_2 , 24.0% of Fe_2O_3 , quenched from 1450°C .

(B) Upper—Pattern of composition consisting of 53.9% of CaO , 15.3% of Al_2O_3 , 6.8% of SiO_2 , 24.0% of Fe_2O_3 quenched from 1450°C . Lower—Pattern of composition consisting of 45.9% of CaO , 7.0% of SiO_2 , 47.1% of Fe_2O_3 quenched from 1540°C . X—Indicate platinum lines.

modification of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ as demonstrated by critical observations of refractive index and by direct studies with pure $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$.

An hypothesis has been proposed to account for the character of the phase premised on the assumption that oxygen polyhedra are formed, giving rise to the periodicity necessary for a strong X-ray pattern, but that the migration of the accessory atoms, necessary to the formation of crystalline compounds, has not occurred. It appears that in these melts the migration of atoms requires an appreciable period of time, and, by the proper choice of temperature, viscosity,

and time interval, an intermediate state of configuration may result wherein the arrangement is no longer entirely random nor the migration complete.

The metastable phase, therefore, may be considered as a mixture of isomorphous units whose chemical formula depends on the original composition of the liquid and the rate of cooling. It may be considered as a continuous structure consisting of oxygen polyhedra with the other atoms in random arrangement between the oxygen atoms. It cannot be considered as an example of the substitution type of solid solution, for in such solutions the structure is an intermediate one between the end members. The similarity of the X-ray diffraction pattern to that of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ may be accidental, since both $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and the metastable phase are built of units of approximately the same dimensions, or it may be that the relationship is more fundamental.

In Portland cement clinker, which is never cooled instantaneously, it seems that true glasses are not likely to be present, that is, in the sense that the under-

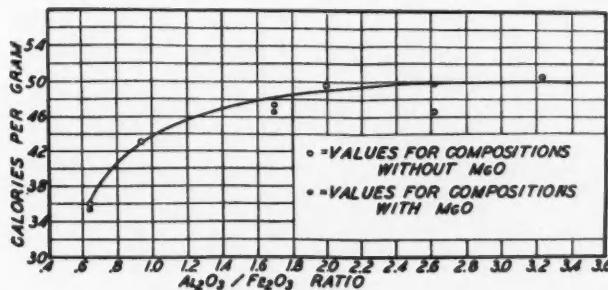


Fig. 1.—Latent Heat of Crystallisation of Liquid Compositions of varying Alumina : Ferric Oxide Ratios on the Tricalcium Silicate-Dicalcium Silicate surface at 1400° C.

cooled solidified liquid shows no X-ray diffraction lines. However, a part of the interstitial material in clinker (the material which was liquid at the burning temperature) may remain essentially one phase having the composition of the liquid and this is the material which is referred to herein as "glass."

It should be pointed out that the above observations have indicated that the identification of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ by means of the X-ray pattern is not feasible.

Approximation of Glass Content.—Although the microscopic examination of polished sections of clinker, as previously set out, has revealed an amorphous interstitial phase, the lack of a confirming method for estimating the glass content has seriously curtailed research on that phase. Recognising that heat is liberated when glass changes to the more stable crystalline state, a method has been reported by Lerch for the approximation of the glass content of clinker which is based on the latent heat of crystallisation of the glass.¹⁸ Liquid compositions were prepared of $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ ratios from 0.64 to 3.24 on the $3\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{CaO} \cdot \text{SiO}_2$ surface on the 1,400 deg. isotherm. The latent heats of crystallisation were determined by noting the differences in the heats of solution of these preparations

following heat treatments such as to produce, on the one hand, complete crystallisation and, on the other hand, complete undercooling and solidification wholly as glass. After correcting for the heat of inversion of β - to γ - $2\text{CaO} \cdot \text{SiO}_2$ (inversion occurred in the slowly cooled, completely crystalline charge) a curve was drawn (Fig. 1) representative of the latent heats of crystallisation of liquid compositions throughout the range of Portland cements. Now if a specimen of clinker were tested for its heat of solution, and a duplicate specimen similarly tested following a heat-treatment designed to produce complete crystallisation, then the difference between the two values, properly corrected, represents the latent heat of crystallisation of the glass in the clinker. The value divided by the latent heat of crystallisation of a pure glass of the same $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ ratio (taken from the curve) gives the fractional part of glass in the clinker.

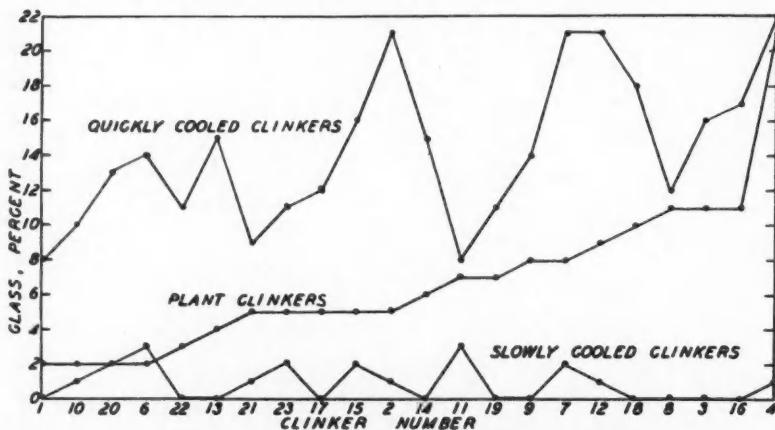


Fig. 2.—The Approximated Glass Contents of Clinkers arranged in order of increasing Glass Content of the Plant Clinkers.

At present the method is regarded as only a rough approximation, since certain assumptions are made which are subject to modification. It is assumed, for example, that the glass in a cement clinker has the same $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ ratio as the clinker itself, and that it is located on the 1,400 deg. isotherm on the $3\text{CaO} \cdot \text{SiO}_2-2\text{CaO} \cdot \text{SiO}_2$ surface. This cannot be true if the amount of glass is less than that expected at 1,400 deg. Another source of error is in the latent heats of crystallisation, determined on liquid compositions which, by themselves, do not yield the same crystalline product as when present in clinker.

The chief difficulty in the way of securing an accurate method of estimating glass content is in the lack of knowledge concerning the character of the course of crystallisation in commercial clinker, whether normal or independent. An investigation intended to take into account the change in the $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ ratio of the liquid during crystallisation is contemplated. When the method is modified to eliminate or reduce the error from this source, it may be possible to

obtain a clue as to the character of the course of crystallisation, through comparisons of calculated values with microscopic observations.

The results, however, are significant of definite changes induced in a clinker by the heat-treatment and probably are correctly interpreted as an expression of glass content. Although the order of reproducibility is such as to indicate a high precision, the uncertainties in interpretation suggest a conservative estimate of the absolute accuracy of the methods, perhaps in the order of ± 5 per cent.

TABLE I.—THEORETICAL EQUILIBRIUM COMPOSITION AND APPROXIMATED GLASS CONTENT OF COMMERCIAL CLINKER TREATED AS INDICATED. S = CLINKER REHEATED AND COOLED SLOWLY. P = PLANT CLINKER AS RECEIVED. Q = CLINKER REHEATED AND COOLED SLOWLY.

No.	A/F Ratio	Theoretical Equilibrium Composition ¹										
		C ₃ S	C ₂ S	C ₃ A	C ₄ AF	MgO	Free CaO			Glass Content		
							S	P	Q	S	P	Q
1	2.9	50	24	12	7	3.0	0.4	1.2	1.5	0	2	8
2	1.1	56	17	6	17	1.8	0.1	0.8	0.9	I	5	21
3	2.2	49	28	10	7	4.0	0.2	0.4	0.4	0	11	16
4	0.8	48	20	4	16	4.2	0.3	4.2	1.6	I	21	22
5	0.8	54	26	1	14	1.6	0.1	0.3	0.4	—	—	—
6	2.0	61	17	10	9	1.4	0	0.4	0.5	3	2	14
7	3.0	50	23	14	7	3.4	tr.	0.4	0.6	2	8	21
8	1.8	52	25	8	9	3.5	0.1	0.6	0.8	0	11	12
9	2.7	42	33	11	7	4.2	0.1	0.8	0.9	0	8	14
10	1.8	41	37	8	9	1.3	0.2	2.1	2.0	I	2	10
11	1.0	54	15	4	16	0.8	0.1	0.2	0.3	3	7	8
12	0.8	48	27	3	19	2.4	0	tr.	0.1	I	9	21
13	2.1	53	23	10	8	4.3	0.1	0.4	0.6	0	4	15
14	2.1	54	22	9	8	3.9	tr.	0.9	0.8	0	6	15
15	1.9	47	27	9	9	4.2	0.1	1.3	1.4	2	5	16
16	2.4	50	26	12	7	3.3	0	0.4	0.3	0	11	17
17	2.4	53	26	11	8	1.3	0.2	0.4	0.5	0	5	12
18	2.3	52	23	12	6	3.6	0.1	0.8	0.5	0	10	18
19	1.9	49	27	9	9	4.7	tr.	0.6	0.5	0	7	11
20	1.9	60	12	12	12	1.0	0.3	1.3	1.4	2	2	13
21	2.5	56	18	14	9	1.3	0.1	0.4	0.4	I	5	9
22	2.3	48	26	11	8	4.4	0	0.3	0.2	0	3	11
23	3.0	56	15	15	7	3.1	0.9	2.0	1.6	2	5	11

¹ The usual abbreviations for the chemical symbols are used in TABLES and FIGURES. C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, M = MgO, N = Na₂O, K = K₂O. Hence, C₄A = 3CaO · Al₂O₃, etc.

Composition at Arrested Crystallisation.—As a part of a research on the effects of glass in clinker on the properties of the cement, a special study has been made of the glass content of 22 commercial clinkers obtained from plants in the United States selected to include a wide variation in composition and treatment. A portion of each clinker³¹ was reheated to about 1,400 deg. and cooled slowly (designated S samples) in order to obtain a minimum of glass; another portion

TABLE 2.—COMPARISON OF COMPOUND CONTENTS.
(This Table is concluded on page 239.)

%	Complete Equilibrium Crystallization	Crystallization at Eutectic Liquid gives Glass	Crystallization at Quintuple Line. Liquid gives Glass	Crystallization at Quintuple Line. Liquid crystallizes independently
I. CaO = 68.0%; SiO ₂ = 23.0%; Al ₂ O ₃ = 6.0%; Fe ₂ O ₃ = 3.0%. A/F = 2				
C ₂ S.....	57.5	57.3	60.6	60.6
C ₂ S.....	22.5	19.5	15.8	20.3
C ₂ A.....	10.8	4.9	0	8.6
C ₄ AF.....	9.1	0	0	9.1
CaO.....	0	0	0	0
C ₂ A ₃	0	0	0	1.5
Glass.....	0	18.3	23.4	0
II. CaO = 68.0%; SiO ₂ = 23.0%; Al ₂ O ₃ = 7.0%; Fe ₂ O ₃ = 2.0%. A/F = 3.5				
C ₂ S.....	52.2	52.1	59.5	59.5
C ₂ S.....	26.5	24.5	15.7	21.0
C ₂ A.....	15.2	11.2	0	8.6
C ₄ AF.....	6.1	0	0	6.2
CaO.....	0	0	0	0
C ₂ A ₃	0	0	0	4.7
Glass.....	0	12.2	24.7	0
III. CaO = 66.0%; SiO ₂ = 24.0%; Al ₂ O ₃ = 7.5%; Fe ₂ O ₃ = 2.5%. A/F = 3				
C ₂ S.....	32.4	32.3	39.0	39.0
C ₂ S.....	44.5	42.0	34.8	40.4
C ₂ A.....	15.7	10.7	0	9.4
C ₄ AF.....	7.6	0	0	7.6
CaO.....	0	0	0	0
C ₂ A ₃	0	0	0	4.4
Glass.....	0	15.3	27.1	0
IV. CaO = 67.0%; SiO ₂ = 23.0%; Al ₂ O ₃ = 4.0%; Fe ₂ O ₃ = 6.0% ¹ . A/F = 0.67				
C ₂ S.....	62.7	62.3	58.9	63.6
C ₂ S.....	18.6	18.4	18.1	18.1
C ₂ A.....	0.5	0	0	0.4
C ₄ AF.....	18.2	17.6	0	18.2
CaO.....	0	0	0	0.2
C ₂ A ₃	0	0	0	0
Glass.....	0	1.5	22.6	0

¹ In this case, free lime is produced when the liquid crystallizes independently. If this is estimated analytically, the Bogue calculation will give the values appearing under "Liquid crystallizes independently."

TABLE 2 (contd.).—COMPARISON OF COMPOUND CONTENTS.

%	Crystallization at 1400° Liquid gives Glass	Crystallization at 1400° Liquid crystal- lizes indepen- dently	Crystallization at 1450° Liquid gives Glass	Crystallization at 1450° Liquid crystallizes independently
I. CaO = 68.0%; SiO ₂ = 23.0%; Al ₂ O ₃ = 6.0%; Fe ₂ O ₃ = 3.0%. A/F = 2				
C ₃ S.....	59.6	59.6	59.6	59.6
C ₂ S.....	16.2	21.2	15.6	21.0
C ₃ A.....	0	8.9	0	9.8
C ₄ AF.....	0	9.1	0	9.1
CaO.....	0	0	0	0
C ₅ A ₃	0	1.0	0	0.5
Glass.....	24.3	0	24.8	0
II. CaO = 68.0%; SiO ₂ = 23.0%; Al ₂ O ₃ = 7.0%; Fe ₂ O ₃ = 2.0%. A/F = 3.5				
C ₃ S.....	60.6	60.6	59.4	59.4
C ₂ S.....	15.4	20.9	15.3	21.4
C ₃ A.....	0	9.4	0	9.7
C ₄ AF.....	0	6.1	0	5.9
CaO.....	0	0	0	0
C ₅ A ₃	0	3.8	0	3.8
Glass.....	25.1	0	25.5	0
III. CaO = 66.0%; SiO ₂ = 24.0%; Al ₂ O ₃ = 7.5%; Fe ₂ O ₃ = 2.5%. A/F = 3				
C ₃ S.....	38.2	38.2	38.5	38.5
C ₂ S.....	34.3	40.2	33.3	39.9
C ₃ A.....	0	10.5	0	10.6
C ₄ AF.....	0	7.6	0	7.6
CaO.....	0	0	0	0
C ₅ A ₃	0	3.6	0	3.5
Glass.....	27.6	0	28.1	0
IV. CaO = 67.0%; SiO ₂ = 23.0%; Al ₂ O ₃ = 4.0%; Fe ₂ O ₃ = 6.0%. A/F = 0.67				
C ₃ S.....	54.6	60.9	55.1	61.5
C ₂ S.....	20.2	20.2	19.4	19.4
C ₃ A.....	0	0.4	0	0.5
C ₄ AF.....	0	18.2	0	18.2
CaO.....	0	0.3	0	0.7
C ₅ A ₃	0	0	0	0
Glass.....	25.0	0	25.5	0

was reheated and cooled quickly (designated *Q*) to obtain a maximum of glass ; a third portion was taken from the plant clinker as received (designated *P*).

The glass content of each of the differently treated clinkers was approximated by the method given above.⁴⁴ The results are tabulated in *Table I* and are shown graphically in *Fig. 2*, arranged in order of increasing glass content of the plant clinkers. Two points stand out clearly from these tests : (1) The glass content of the commercial clinkers as received varies over a wide range, from 2 to 21 per cent., and (2) The glass content is definitely affected by the heat-treatment, that is, by the rate of cooling of the clinker. The glass in the quickly-cooled clinkers varied between 8 and 22 per cent. ; that in the slowly-cooled clinkers between 0 and 3 per cent.

Forsén⁴⁵ pointed out five years ago that the time element in the recrystallisations, necessary in the systems of Portland cement in order to attain continuous equilibrium at the liquidus, is so great that it is unlikely that a state of equilibrium obtains in any commercial clinker. Thus, in the system $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, the composition that has been known as "Jäneckite," $8\text{CaO} + \text{Al}_2\text{O}_3 + 2\text{SiO}_2$, forms on slow cooling⁴⁶ $3\text{CaO} \cdot \text{SiO}_2 + 2\text{CaO} \cdot \text{SiO}_2 + 3\text{CaO} \cdot \text{Al}_2\text{O}_3$. The primary phase is $3\text{CaO} \cdot \text{SiO}_2$ which separates while the residual melt changes along a line from $3\text{CaO} \cdot \text{SiO}_2$ through $8\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ until the field of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is reached. Then $3\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ separate until, at 1,455 deg., point 16 (invariant point for $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$) is reached.⁴⁷ On continued slow cooling, some $3\text{CaO} \cdot \text{SiO}_2$ is then dissolved and $2\text{CaO} \cdot \text{SiO}_2$ separates with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. But, if the cooling is rapid, this secondary transformation does not occur and the residual melt at point 16 may either solidify as a glass or it may crystallise without the resolution of the $3\text{CaO} \cdot \text{SiO}_2$. The probable product on rapid cooling is $3\text{CaO} \cdot \text{SiO}_2 + \text{glass}$.

When ferric oxide was added, $3\text{CaO} \cdot \text{SiO}_2$, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and glass were believed to result and, with larger amounts of silica, $2\text{CaO} \cdot \text{SiO}_2$ also crystallised out. This reasoning led Forsén to the establishment of an upper lime limit (the weight ratio between CaO and the Al_2O_3 after allowing for $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$) which varied with the composition between 1 and 1.65, but usually was about 1.18.

Lea and Parker⁴⁸ have calculated the compound compositions which may result from differences in the course followed by the liquid in solidification. They have calculated (*Table 2*) the theoretical composition of four clinkers under 8 conditions of hypothetical cooling, including the equilibrium crystallisation ; crystallisation at the eutectic with liquid-forming glass ; and crystallisation at the quintuple line, at 1,400 deg. and 1,450 deg. respectively with liquid-giving glass and with liquid crystallising independently in each case. Other temperatures of reference could be selected for study from their data.

(*To be continued.*)

⁴⁴ LERCH, WM. *Bur. St. J. Res.*, 1938, 20, 77; RP 1066.

⁴⁵ FORSÉN, L. *Zement*, 1935, 24, 17, 33, 77, 139, 191. (First presented at Tech. High School of Zurich, June 17, 1933.) Translated in part in *Concrete* (Cement Mill Ed.), 1937, 45, 231, 250.

⁴⁶ HANSEN, C. W., DYCKERHOFF, W., ASHTON, F. W., & BOGUE, R. H. *J. Phys. Chem.*, 1927, 31, 607.

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